

PAPER • OPEN ACCESS

Two different types of ferromagnetic state in TiO_2 -Co nanopowders

To cite this article: M A Uimin *et al* 2019 *J. Phys.: Conf. Ser.* **1389** 012046

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing together innovative digital publishing with leading authors from the global scientific community.

Start exploring the collection—download the first chapter of every title for free.

Two different types of ferromagnetic state in TiO₂-Co nanopowders

M A Uimin^{1,2}, D V Privalova¹, A S Volegov², A S Minin^{1,2}, A S Konev¹, A Ye Yermakov^{1,2} and V S Gaviko^{1,2}

¹ M.N.Miheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, 620108, Ekaterinburg, Russia

² Ural Federal University n.a. the First President of Russia B.N. Yeltsin, 620002, Ekaterinburg, Russia

E-mail: uimin@imp.uran.ru

Abstract. TiO₂-Co nanopowders were synthesized by the sol-gel method and gas condensation method. The structure of powders and its change during various heat treatments in air and hydrogen was investigated. The samples obtained by the gas condensation method contain ferromagnetic regions in the as-prepared state. This ferromagnetism does not disappear when annealed in air at 773 K. The magnetization curves of these powders are measured in the temperature range from 2 up to 773 K and the temperature dependence of the ferromagnetic contribution is analyzed.

1. Introduction

The origin of ferromagnetism in oxides with small additions of 3d-elements or even without them is the subject of numerous discussions [1]. Due to the small amount of dopant, the presence or absence of a second magnetic phase is difficult to establish using XRD and TEM methods, which are usually used to analyze a structural state. In this paper, we present the results of measuring magnetic properties in the temperature range from 2 to 773 K. The sensitivity of magnetic methods for detecting small amounts of a substance in a ferromagnetic state is significantly higher than the sensitivity of structural methods, which makes it possible to investigate substances with a very low concentration of carriers of magnetic moments, at the level of tens of ppm. Since in heterogeneous systems magnetic carriers can be in different magnetic states, the magnitude of the magnetization itself cannot yet characterize the nature of the carrier of the magnetic moment. In the case of noninteracting magnetic carriers, value of the moment can be determined from the magnetization curve at low temperatures by comparison with the calculation. The second method is the analysis of the temperature dependence of susceptibility, which must obey the Curie law. In the most interesting for us case of interacting moment carriers, in principle, two main characteristics of a ferromagnet — the saturation magnetization M_s and the Curie temperature T_C — can be used to identify the magnetic impurity. The magnetic moment of the sample can be measured with very high accuracy, but for heterogeneous samples, the problem arises as to which part of the entire sample corresponds to the measured moment. If this volume fraction is unknown, it is impossible to determine the magnetization M_s of the magnetic fraction of the sample. As noted in [2], [3], difficulties arise in the analysis of saturation fields, which are uniquely related to the magnetization only for noninteracting multidomain particles.



For small particles, the saturation field is close to the value of K/M_s , where K is the constant of magnetocrystalline anisotropy [3]. The lack of information about the anisotropy constant in these cases makes it impossible to identify the magnetic material by analyzing the saturation field. Thus, the Curie temperature T_C remains one of the few experimentally available parameters characterizing the nature of the magnetic material. The T_C value does not depend on the structural state and the particle size of iron, cobalt, and nickel up to several nanometers [4]. The temperature dependence of the magnetization of a substance containing particles of metallic cobalt should be radically different from other ferromagnets, and this makes it possible to detect such states in titanium oxides doped with cobalt.

2. Experimental

In this work, titanium oxide nanopowders with cobalt additives were synthesized by two methods - using sol-gel synthesis (S-G), as well as using gas condensation synthesis (GC). The latter method is characterized by the production of non-equilibrium states with a large number of defects, which are believed to be associated with the appearance of ferromagnetic ordering in the $\text{TiO}_2\text{-Co}$ systems. The used sol-gel method is based on the technique reported at [5, 6]. Titanium isopropyl oxide and cobalt acetylacetonate (both Sigma Aldrich, USA) were used as precursors. After synthesis, the powders were annealed in air at 673 K for 2 hours to remove the remaining traces of organic contaminants and water. Chemical analysis of the sample revealed that the content of cobalt is 1.8 wt.% (2.4 at.%). GC $\text{TiO}_2\text{-Co}$ nanopowders were produced by evaporation of overheated (~ 2300 K) liquid drop of Ti in the flow of inert gas (Ar) containing oxygen as described in our earlier paper [7]. Two technological schemes for the gas condensation synthesis of nanopowders were used: - with Ar: O₂ ratio of 200:1 (GC-1 powders) and 16:1 (GC-2 powders). The mixture of Ti and Co powders was used as a precursor. The content of cobalt in the GC powders was 2,78 wt.% (4 at.%). The structure of the nanopowders was investigated using a PANalytical Empyrean high-resolution X-ray diffractometer in filtered copper radiation by scanning at a step of 0.013 degrees. The microstructure was studied using a Tecnai G2 30 Twin transmission microscope. Magnetic measurements were carried out using SQUID magnetometer (at 2-300 K) and Faraday balance magnetometer (at 293-773 K).

3. Results

It was found that the powders synthesized by the sol-gel method have anatase structure, and the powders obtained by the gas-phase method contain 60% rutile and 40% anatase (figure1).

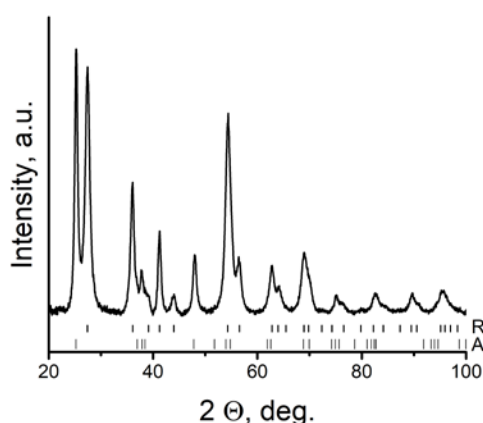


Figure 1. X-ray diffraction pattern of GC-1 $\text{TiO}_2\text{-Co}$ powder.

Figure 2 shows the electron microscopy images of the GC-1 powder. The particle size ranged from 10 to 50 nm. Annealing at 773 K did not lead to a noticeable change in the size and shape of the GC-1 powder particles (figure 2a and 2b).

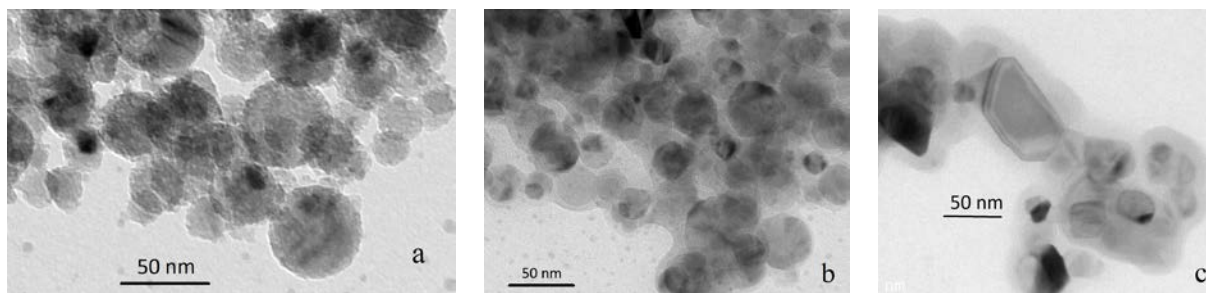


Figure 2. Electron microscopy image of GC-1 $\text{TiO}_2\text{-Co}$ powder before (a) and - after annealing 2 hrs in air at 773 K(b). (c) -TEM micrographs of GC-1 $\text{TiO}_2\text{-Co}$ nanopowder after annealing 2 hrs in hydrogen at 973 K.

After annealing in hydrogen at 973 K, the faceting appears, and all particles are covered with a structureless low contrast phase (figure 2 c). Probably, the surface of the particles is amorphous, since haloes characteristic of the amorphous state appear on the electron diffraction patterns. The appearance of an amorphous layer on the surface of particles during hydrogen treatment was noted in [8].

A noticeable ferromagnetic contribution to the magnetization curve in the state immediately after the synthesis was observed only in one case — with the first gas condensation synthesis scheme (GC-1 powders). The magnitude of the magnetization obtained by extrapolation to a zero field at 300 K was 0.4 emu/g (figure 3, inset). In the remaining cases, annealing in vacuum or hydrogen was carried out to obtain the ferromagnetic state. The hydrogen annealing of the GC-1 $\text{TiO}_2\text{-Co}$ powder at 973 K resulted in a high magnetization value of 4 emu/g, which can be explained by the formation of a cobalt metal phase. EDX analysis in TEM studies showed the presence of areas with a high cobalt concentration (tens percent). Apparently, in this case, both the cobalt particle and the matrix turned out to be in the probe region at the same time; therefore, the observed local cobalt concentration was not 100%.

The most intriguing is the partial preservation of the ferromagnetic state of GC-1 powders during annealing in air at 773 K 2 hrs (figure 3).

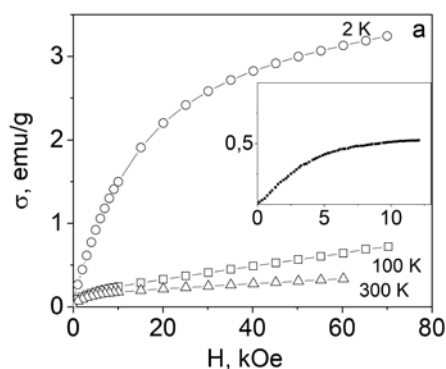


Figure 3. Magnetization curves of GC-1 $\text{TiO}_2\text{-Co}$ nanopowder after annealing in air at 773 K 2 hrs, measured at 2 K, 100 K and 300 K. The inset shows the magnetization curve of GC-1 sample at 300 K immediately after synthesis.

Measurements of the magnetization curves of this sample were also carried out in air and showed complete reversibility in the interval from 293 to 773 K (curves 293-1 and 293-2 in figure 4). The temperature dependence of ferromagnetic contribution, determined by extrapolation to the zero fields, is shown in figure 5. As can be seen from figure 5, the temperature dependence of the magnetization of the GC-1 $\text{TiO}_2\text{-Co}$ powder after annealing at 773 K in the air 2 hrs (curve 1) differs significantly from that for bulk cobalt. Note that the temperature dependence of the magnetization of the as synthesized GC-1 powder turned out to be close to that shown in figure 5, curve 1, except for a slight irreversible decrease in the magnetization during measurements.

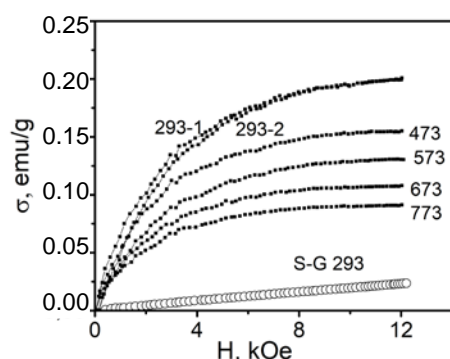


Figure 4. Magnetization curves of GC-1 TiO₂-Co nanopowder, annealed in air at 773 K 2 hrs. 293-1 – before heating, 293-2 – after heating up to 773 K. Open symbols – S-G TiO₂-Co nanopowder at 293 K.

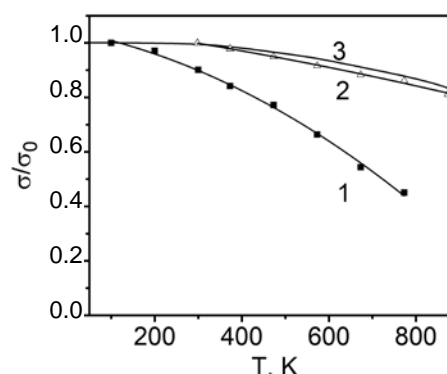


Figure 5. Temperature dependences of magnetization of GC-1 TiO₂-Co nanopowders (1) after air annealing at 773 K 2 hrs, (2) after annealing at 973 K 2 hrs in hydrogen. (3) – bulk Co. Magnetization value is reduced to value at 100 K for (1, 3) and 293 K for (2).

We checked whether the rapid decrease in magnetization is not a manifestation of possible superparamagnetism of small cobalt regions. It is known that the magnetization curves of a superparamagnetic at a different temperatures should be on one master curve in the coordinates $M-H/T$. Plotting in $M-H/T$ coordinates (figure 6) showed that temperature changes in the magnetization curves could not be described within the superparamagnetic model.

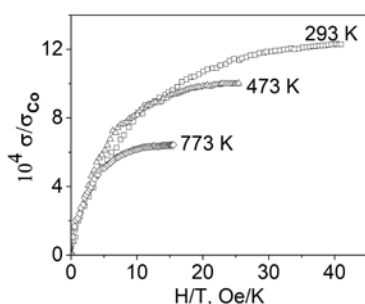


Figure 6. Magnetization curves of GC-2 TiO₂-Co nanopowder, measured in air at 293 K, 473 K, and 773 K as a function of H/T .

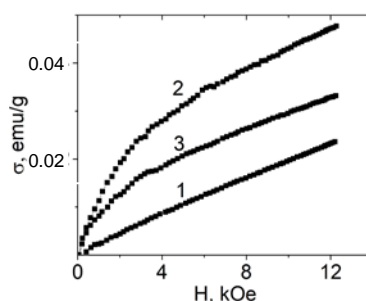


Figure 7. Magnetization curves of S-G TiO₂-Co nanopowders at 293 K. (1) – as-prepared state, (2) - after one cyclic heat treatment + annealing in hydrogen at 573 K 6 hrs, (3) – after two cyclic heat treatment.

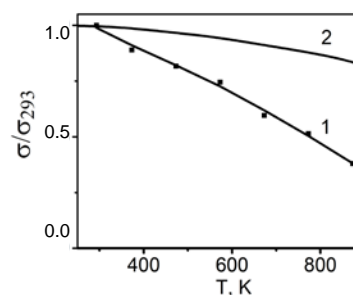


Figure 8. Temperature dependences of magnetization of S-G TiO₂-Co nanopowder after 2 cycles of heat treatment (1). 2 – bulk Co.

At the same time, GC-1 powder after annealing in a hydrogen atmosphere at 973 K (figure 5, curve 2) demonstrated a temperature dependence of the magnetization identical to cobalt (curve 3). It should be noted that the magnetization of the samples annealed in hydrogen drops to almost zero when heated in air, therefore, in this case, the measurements were carried out in a medium (Ar-5% H₂). Both of these facts — different temperature dependences of $M(T)$ and unusual resistance to annealing in air — suggest that in the process of gas condensation synthesis, regions with a particular unique structural state, with a high temperature of magnetic ordering, are formed on the surface of the nanoparticles, but

these regions are not cobalt particles. Since this particular structural state is formed during the condensation of metal vapors in an atmosphere with a low oxygen concentration, it can be assumed that vacancies along the oxygen sublattice play a vital role in the formation of this ferromagnetic state, as shown in [9]. In papers [9, 10], the paramagnetic-ferromagnet transformation in $\text{TiO}_2\text{-Co}$ nanopowders obtained by the sol-gel method is discussed. The ferromagnetic state occurs after annealing in hydrogen at 573 K or 673 K. Subsequent annealing in the air again leads to a paramagnetic state. These reversible changes in the magnetic state are repeated during subsequent cycles of heat treatments. We carried out such heat treatments on S-G powders and also observed the appearance of a ferromagnetic state after annealing in hydrogen at 573 K. Just as the authors of [9] described it, we carried out two cycles of heat treatments, each of which consisted of annealing in hydrogen at 573 K, followed by annealing in air at 673 K (figure 7). The duration of each annealing was 6 hours. Annealing in air at 673 K led only to a partial decrease of the ferromagnetic contribution to the magnetization (figure 7, curve 3), and not to its complete disappearance, as noted in Ref.[9].

The temperature dependence of the ferromagnetic contribution to the magnetization was measured exactly as described above for sample GC-1. It turned out that the temperature dependence of this value also differs from the dependence characteristic of cobalt (figure 8).

We were unable to determine the Curie temperature of GC and SG powders in a ferromagnetic state due to changes in the structure of powders beginning at high temperatures. It can only be noted that for our powders, these values significantly exceed the value of T_C defined in [9, 10] as 470 K. At present, there is no generally accepted model explaining the ferromagnetic state in such objects. Therefore, the reasons for the differences in T_C for different samples are not clear. The positive moment of this whole story of obtaining the ferromagnetic state in $\text{TiO}_2\text{-Co}$ nanopowders is that the heat treatment proposed by the authors [9, 10] in our case led to similar results.

4. Conclusions

Magnetic properties of $\text{TiO}_2\text{-Co}$ nanopowders were studied both in as-prepared state and after heat treatments. The analysis of magnetization curves at temperatures from 2 to 773 K showed that two types of ferromagnetic phase could be realized. One type of ferromagnetic phase is metallic cobalt with the typical temperature dependence of magnetization. The second type of ferromagnetic phase is characterized by a completely different dependence $M(T)$ and high stability when heated in an oxidizing atmosphere.

Acknowledgments

X-ray studies and electron microscopy was carried out using the equipment of the Collaborative Access Center “Testing Center of Nanotechnology and Advanced Materials” IMP. This work was carried out within the state assignment of Minobrnauki of Russia (themes “Alloys” and “Magnet”).

References

- [1] Coey J M D and Chambers S A 2008 *MRS Bull.* **33** 1053
- [2] Coey J M D, Mlack J T, Venkatesan M and Stamenov P 2010 *IEEE Trans. Magn.* **46** 2501
- [3] Kittel C 1998 *J. Geophys. Res. Solid Earth* **103** 30533
- [4] Bills I M L, Chatelain A and De Heer W A 1997 *J. Magn. Magn. Mater.* **168** 64
- [5] Sharma S, Chaudhary S, Kashyap S C and Sharma S K 2011 *J. Appl. Phys.* **109** 083905
- [6] Uymin M A et al 2019 *Lett. Mater.* **9** 91
- [7] Sokolov V I, Druzhinin A V, Kim G A, Gruzdev N B, Yermakov A Ye, Uimin M A, Byzov I V, Shchegoleva N N, Vykhodets V B and Kurenykh T E 2013 *Physica B* **430** 1-5
- [8] Xiaobo C, Lei L, Peter Y and Yu S S M 2011 *Science* **331** 746
- [9] Manivannan A, Glaspell G, Dutta P and Seehra M S 2005 *J. Appl. Phys.* **97** 10D325
- [10] Manivannan A, Glaspell G and Seehra M S 2003 *J. Appl. Phys.* **94** 6994